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Effect of pyrosulphate ion on the surface tension of surfactants in aqueous acetone media

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Abstract Surface tensions of solutions of sodium dodecyl sulphate (S.D.S.), cetyl trimethyl ammonium bromide (C.T.A.B.), potassium pyrosulphate, S.D.S. and C.T.A.B. in presence of pyrosulphate ion in water and water + acetone ($X_{acetone}$ = 0.016, 0.033, 0.072 and 0.117) mixtures have been measured by means of the ring detachment method at 298.15, 303.15, 308.15 and 313.15 K. The data were analyzed using the Gibbs equation and various thermodynamic functions have been evaluated. The results reveal the nature of solute adsorption at the interface in these solutions.

Keywords . Interfacial tension, thermodynamic functions, surfactants

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1. Introduction

Solutes such as ionic salts [1] usually increase the surface tension of aqueous solution above the value of pure water and in such solution, the surface layers are poorer in that solute. Analysis of experimental data using the Gibbs equation results in a negative surface excess concentration of the solute at the interface (*i.e.* negative adsorption). On the other hand, surface active agents such as fatty acids [2], containing both a polar hydrophilic (*e.g.*, –COOH) and a non-polar hydrophobic group (*e.g.*, hydrocarbon residue) lower the surface tension of water and this corresponds to a positive adsorption of the solute at the interface. In continuation of our studies on surface tension of solutions of various electrolytes [3–5] in aqueous and mixed solvent systems, the present work aims at determining the surface tension of S.D.S. and C.T.A.B. in presence of pyrosulphate ion in water and water + acetone mixtures to study the surface properties.

2. Experimental

Sodium dodecyl sulphate, cetyl trimethyl ammonium bromide and potassium pyrosulphate (E Merck, Germany) of AR grade were used as such. Acetone (BDH, AnalaR, containing 0.1% organic impurities and water content of 1%) was purified [6] under reflux with successive quantities of potassium permanganate until the violet colour persisted. It was then dried with anhydrous potassium carbonate filtered from the desiccant fractionated. The water content reduced by storage over a type 4A molecular sieve. Conductivity water (sp. cond. ~10^{-6} cm^{-1}) was used for preparing the water + acetone mixtures of required composition. The acetone content in the mixed solvents was accurate to within ±0.01%. The solutions were prepared on a molal basis by dissolving known weights of the electrolytes in appropriate weights of the relevant solvent. The electrolyte content in the solutions varied over a range of 1×10^{-4} to 5×10^{-4} m for S.D.S. and C.T.A.B., and 1×10^{-2} to 5×10^{-2} m for potassium pyrosulphate. The surface tension of surfactants was further measured in presence of a fixed concentration of potassium pyrosulphate (0.01 m). Surface tension was measured by the ring detachment method using a du Nouy tensiometer (Win. S–53, Winson Co. Calcutta) enclosed in an air thermostat, circulating water from a thermostatically regulated bath around the sample holder with double wall to maintain the temperature of the solution, constant with a precision of ±0.05 K. Before each measurement, the platinum ring was cleaned by flaming and the surface of the liquid was blown off by a capillary. The planarity of the ring was

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checked by viewing its mirror image in the surface of the liquids. The calibration of tensiometer was made by using the surface tension values of pure water at the experimental temperatures as available in the literature [7]. At least five observations were made for each solution and the average was taken as the final surface tension value of the concerned solution.

Conductance measurements were carried out on a digital conductivity meter (Systronics, type 304) with a sensitivity of 0.1% and a dipping type conductivity cell with platinized electrodes (cell constant 1 S cm ^{1}).

3. Results and discussion

The values of surface tension (γ) were measured for the solutions of S.D.S., C.T.A.B., $K_2S_2O_7$, S.D.S. and C.T.A.B. in presence of $S_2O_7^{2-}$ in water and water + acetone mixtures at 298.15, 303.15, 308.15 and 313.15 K. Typical plots that show the variation of γ with the square root of the molality are shown in Figure 1.

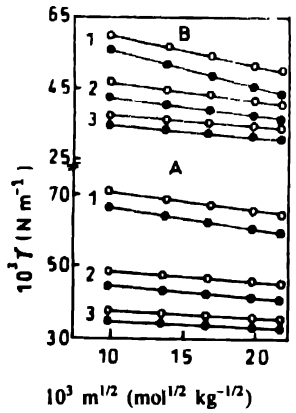

Figure 1. Plot of γ *vs* $m^{1/2}$ for (A) S.D.S. (0–0), C.T.A.B. (●–●), (B) S.D.S and C.T.A.B in presence of $S_2O_7^{2-}$ in (1) $X_{acetone} = 0.00$, (2) $X_{acetone} = 0.033$ and (3) $X_{acetone} = 0.117$ at 298.15 K.

As observed the surfactants lower the surface tension of water indicating that the surface layers of the solutions are enriched in the corresponding solute. The lowering of surface tension is again noticed by increasing the concentration and temperature. This qualitative picture leads to the conclusion that the surfactants under study can be said to be positively adsorbed at the interface. The positive adsorption is further strengthened in presence of $S_2O_7^{2-}$ and by increasing the acetone content in water. The lowering of surface tension is more marked in C.T.A.B. than in S.D.S. in all the solvents and at all temperatures.

The stoichiomolalities (m) have been converted to mean ionic activities ($a_\pm$) using the mean ionic activity coefficient ($\Upsilon_\pm$) as follows :

$$a_\pm = Q\alpha m \Upsilon_\pm, \tag{1}$$

where $Q = (\nu_+^{\nu_+}\nu_-^{\nu_-})^{1/\nu}$ and $\nu = (\nu_+ + \nu_-)$ is the total number of moles of ions (ν_+ is the number of moles of positive ions and ν_- is the number of moles of negative ions) given by 1 mole of the solute and α is the degree of dissociation of the solute obtained from the conductance measurements [8–11]. The mean ionic activity coefficient ($\Upsilon_\pm$) was determined by means of the Debye-Hückel limiting law

$$\log \Upsilon_\pm = -S|z_+z_-|I^{1/2}, \tag{2}$$

where z_+ and z_- are the valencies of the positive and negative ions, respectively, S is the Debye-Hückel constant and is given by $1.823 \times 10^6/(DT)^{3/2}$, and I is the ionic strength of the solution given by

$$I = 1/2\sum m_i z_i^2 = 1/2\left[(m\alpha z_+^2\nu_+) + (m\alpha z_-^2\nu_-)\right]. \tag{3}$$

Assuming that Gibbs equation applies to the above solutions, the surface excess (Γ_2) can be obtained from

$$\Gamma_2 = -a_\pm/2RT(d\gamma/da_\pm) \tag{4}$$

or $$\Gamma_2 = -1/2.3026\, RT(d\gamma/d\log a_\pm)_T, \tag{5}$$

where $a_\pm$ is the bulk mean ionic activity as evaluated by means of eq. (1), and $d\gamma/da_\pm$ and $d\gamma/(d\log a_\pm)$ are the slopes of the plots of γ *vs* $a_\pm$ (Figure 2) and γ *vs* $\log a_\pm$ (Figure 3), respectively.

It is evident from Figures (1–3) that the variation of γ with molality or mean ionic activity is invariably similar at all temperatures. Therefore, $d\gamma/da_\pm$ is independent of temperature. Keeping this simplification in mind, we can write

$$d\Gamma_2/dT = a_\pm/2RT^2(d\gamma/da_\pm). \tag{6}$$

Considering the model as adapted [1] to apply to the present data, an alternative expression for the temperature coefficient of Γ_2 can be written in the form

$$d\Gamma_2/dT = a_\pm/RT^2\ \Delta H^0\ \tau, \tag{7}$$

where τ is the thickness of the surface phase existing in equilibrium with the bulk phase and ΔH^0 is the change in standard enthalpy in transferring 1 mole of the solute from the bulk to the surface region, neglecting temperature variation. Comparing eq. (6) with eq. (7) we obtain

$$d\gamma/da_\pm = 2\ \Delta H^0\ \tau, \tag{8}$$

which enables us to determine the values of ΔH^0, provided that the value of τ is known. However, in the absence of any definite knowledge about the τ value in the present investigation, the calculation of ΔH^0 presents some difficulties. Consequently, as a measure of good approximation, the value of ΔH^0 was calculated for various

values of τ (τ = 0.5 – 5 nm at intervals of 0.5 nm) from eq (8) at different temperatures for τ = 0.5 nm, a greater linearity of plots of $(d\gamma/da_{\pm})$ *vs* ΔH^0 was observed (*i.e.*, the observed value had the least standard deviation for τ = 0.5 nm as compared to those for other τ values). The change in standard Gibbs free energy (ΔG^0) can be derived by means of

$$\Gamma_2 = -a_{\pm}/RT\ \Delta G^0\ \tau\ . \qquad (9)$$

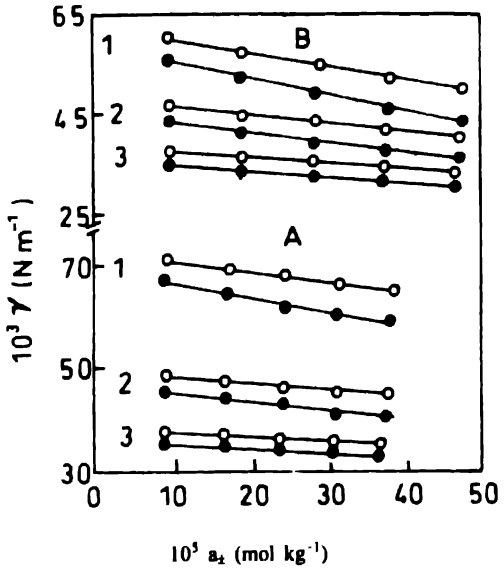

Figure 2. Plot of γ *vs* $a_{\pm}$ for (A) S D S (0–0), C T.A.B (●–●), (B) S D S and C T.A B in presence of $S_2O_7^{2-}$ in (1) $X_{acetone}$ = 0 00, (2) $X_{acetone}$ = 0 033 and (3) $X_{acetone}$ = 0.117 at 298.15 K

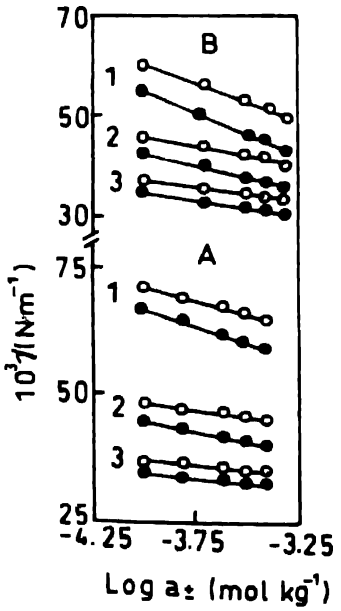

Figure 3. Plot of γ *vs* $\log a_{\pm}$ for (A) S.D.S. (0–0), C.T.A B. (●–●), (B) S.D S and C.T.A.B. in presence of $S_2O_7^{2-}$ in (1) $X_{acetone}$ = 0.00, (2) $X_{acetone}$ = 0.033 and (3) $X_{acetone}$ = 0.117 at 298.15 K.

Finally, the standard entropy change (ΔS^0) was computed from the Gibbs-Helmholtz equation as

$$\Delta S^0 = \left(\Delta H^0 - \Delta G^0\right)/T\ . \qquad (10)$$

The value of Γ_2 (Tables 1–3) are positive in all the solvents and are found to increase in presence of $S_2O_7^{2-}$.

Table 1. Values of the thermodynamic parameters ΔH^0 (kJ mol^{-1}), ΔG^0 (kJ mol^{-1}), ΔS^0 (kJK^{-1} mol^{-1}) and Γ_2 for sodium dodecyl sulphate (S.D S) and S D S in presence of pyrosulphate ion (S D S /$S_2O_7^{2-}$) in water and water + acetone ($X_{acetone}$ = 0 016, 0 033, 0 072 and 0 117) mixtures at different temperatures

$X_{acetone}$	T/K	$10^7\ \Gamma_2$	ΔH^0	ΔG^0	$10^2\ \Delta S^0$
			(S D S)		
0 00	298 15	16 89	–20 79	–93 65	24 44
	303 15	16 63	–20 86	–93 87	24 08
	308 15	16 40	–21 00	–94.27	23.78
	313 15	16 18	–21 48	–94.79	23 51
			(S D S /$S_2O_7^{2-}$)		
	298.15	26 99	–27 93	–135 57	36.44
	303 15	26 55	–27 95	–136 62	35.85
	308 15	26 13	–27 96	–136.67	35 27
	313 15	25 71	–27 98	–136.72	34 72
			(S.D S.)		
0 016	298.15	10 60	–13 78	–58.88	15.13
	303.15	10 44	–13.84	–59.05	14 91
	308 15	10 30	–13 93	–59.34	14 74
	313.15	10 16	–14 05	–59 66	14.56
			(S D S /$S_2O_7^{2-}$)		
	298 15	16 83	–18 60	–85 23	22.35
	303.15	16 56	–18 61	–85.29	21.99
	308 15	16 30	–18 62	–85 35	21 65
	313 15	16 04	–18 64	–85 39	21 31
			(S D S.)		
0 033	298.15	8 75	–10 85	–48 73	12 71
	303.15	8 62	–10 89	–48.85	12.52
	308.15	8 51	10 97	–49 15	12 39
	313.15	8 39	–11.08	–49 41	12.24
			(S D S./$S_2O_7^{2-}$)		
	298.15	13 84	–14 63	–70 18	18 63
	303.15	13 62	–14 64	–70.23	18 34
	308.15	13 41	–14 65	–70.31	18.06
	313 15	13.20	–14.68	–70.38	17 79
			(S.D S.)		
0.072	298 15	6 54	–8 22	–36 63	9.53
	303.15	6.44	–8.26	–36.72	9.39
	308.15	6.37	–8.32	–37.01	9.31
	313 15	6.28	–8.42	–37.22	9 20

Table 1. *(Cont'd.)*

$X_{acetone}$	T/K	$10^7\,\Gamma_2$	ΔH^0	ΔG^0	$10^2\,\Delta S^0$
			(S D.S /$S_2O_3^{2-}$)		
	298.15	10 27	−11 01	−52 24	13 84
	303 15	10 11	−11 02	−52 30	13.62
	308 15	9 96	−11.03	−52 39	13 42
	313.15	9.80	−11 05	−52 43	13 21
			(S D S)		
0 117	298 15	5 05	−6 39	−28 45	7 40
	303 15	4 97	−6 43	−28 57	7 30
	308.15	4 93	−6 48	−28 72	7 22
	313 15	4 86	−6 57	−28 97	7 15
			(S D S /$S_2O_3^{2-}$)		
	298 15	7 86	−8 31	−40.20	10 69
	303.15	7 74	−8 32	−40 23	10 52
	308 15	7.63	−8 33	−40 25	10 36
	313 15	7.51	−8.35	−40 32	10.21

Table 2. Values of the thermodynamic parameters ΔH^0 (kJ mol^{-1}), ΔG^0 (kJ mol^{-1}), ΔS^0 (kJK^{-1} mol^{-1}) and Γ_2 for cetyl trimethyl ammonium bromide (C.T.A.B.) and C T A.B in presence of pyrosulphate ion (C T A B / $S_2O_3^{2-}$) in water and water + acetone ($X_{acetone}$ = 0 016, 0 033, 0 072 and 0 117) mixtures at different temperatures

$X_{acetone}$	T/K	$10^7\,\Gamma_2$	ΔH^0	ΔG^0	$10^2\,\Delta S^0$
			(C.T A B)		
0 00	298.15	22 03	−27 53	−123 11	32.06
	303.15	21.73	−27.78	−123.85	31 69
	308.15	21 47	−28.12	−124 86	31 39
	313.15	21.23	−28 52	−126 04	31 14
			(C T.A.B /$S_2O_3^{2-}$)		
	298.15	31 24	−32 36	−158.06	42 16
	303.15	30 73	−32 38	−158 11	41 47
	308.15	30 24	−32 39	−158 17	40 81
	313 15	29.76	−32.41	−158.23	40.18
			(C.T.A.B.)		
0.016	298.15	13 99	−18.95	−78.26	19 89
	303.15	13.81	−19 13	−78 79	19 68
	308.15	13 65	−19.36	−79 48	19.51
	313 15	13 51	−19 65	−80.33	19.38
			(C T.A B./$S_2O_3^{2-}$)		
	298.15	19.87	−22.19	−100.63	26.31
	303.15	19.55	−22.20	−100.68	25 89
	308.15	19.24	−22.21	−100 74	25 48
	313.15	18 93	−22.24	−100.77	25.08
			(C.T.A.B)		
0.033	298.15	11.63	−15.11	−65.16	16 79
	303.15	11.48	−15.26	−65 60	16.60
	308.15	11.35	−15.47	−66.23	16.47
	313.15	11.24	−15.72	−67 00	16 37

Table 2. *(Cont'd)*

$X_{acetone}$	T/K	$10^7\,\Gamma_2$	ΔH^0	ΔG^0	$10^2\,\Delta S^0$
			(C T A.B /$S_2O_3^{2-}$)		
	298 15	16 53	−18.13	−83 82	22 03
	303 15	16 26	−18 14	−83 85	21 67
	308 15	16 00	−18 15	−83 89	21 33
	313 15	15 75	−18 19	−83 98	21 01
			(C T A B)		
0 072	298 15	8 81	−11 87	−49 56	12 64
	303 15	8 70	−12 01	−49 95	12 51
	308 15	8 60	−12 19	−50 43	12 41
	313 15	8 53	−12 42	−51 14	12 36
			(C T.A B /$S_2O_3^{2-}$)		
	298 15	12.54	−14 00	−63 78	16 70
	303 15	12 33	−14 01	−63 80	16 42
	308 15	12 14	−14 02	−63 86	16 17
	313 15	11 94	−14 05	−63 88	15 91
			(C.T A B.)		
0 117	298 15	6.91	−8 88	−39 06	10 12
	303.15	6 82	−9 01	−39 43	10 03
	308.15	6 75	−9 15	−39 84	9 96
	313 15	6 69	−9 35	−40 40	9 92
			(C T A B /$S_2O_3^{2-}$)		
	298 15	9 84	−10 36	−50 25	13 38
	303.15	9 68	−10 37	−50.28	13 16
	308 15	9 53	−10 38	−50 31	12 96
	313 15	9 38	−10 41	−50 39	12 77

However, the surface excess (Γ_2) decreases with the rise in temperature and with the increase in acetone content. The variation of Γ_2 with mole-fractions of acetone-water mixtures at the temperatures studied can be represented by the empirical relation (Figure 4)

$$\Gamma_2 = A + B(X_{acetone})^{1/2} + C(X_{acetone}), \qquad (11)$$

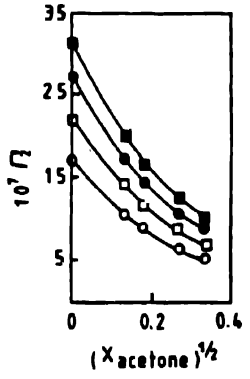

Figure 4. Plot of Γ_2 *vs* $(X_{acetone})^{1/2}$ for S.D S (0–0), C.T.A.B. (□–□), S.D S (●–●) and C.T.A.B. (■–■) in presence of $S_2O_3^{2-}$ at 298.15 K.

where A, B and C are the empirical constants and given in Table 4. Similarly, the variation of Γ_2 with temperature is represented by the relation

$$\Gamma_2 = A' + B'T, \qquad (12)$$

where A' and B' are the constants and are presented in Table 5.

Table 3. Values of the thermodynamic parameters, ΔH^0 (J mol^{-1}), ΔG^0 (J mol^{-1}), ΔS^0 (JK^{-1} mol^{-1}) and Γ_2 for potassium pyrosulphate in water and water + acetone ($X_{acetone}$ = 0.016, 0.033, 0.072 and 0.117) mixtures at different temperatures

X_{ace}	T/K	$10^8\,\Gamma_2$	ΔH^0	ΔG^0	$10^2\,\Delta S^0$
0.00	298.15	33.29	−53.48	−179.31	42.20
	303.15	32.99	−54.49	−181.87	42.02
	308.15	32.71	−55.53	−184.50	41.85
	313.15	32.45	−56.62	−187.26	41.72
0.016	298.15	29.58	−48.54	−162.67	38.28
	303.15	29.31	−49.42	−164.88	38.09
	308.15	29.06	−50.35	−167.25	37.94
	313.15	28.96	−51.94	−170.28	37.78
0.033	298.15	26.14	−45.30	−147.55	34.29
	303.15	25.94	−46.32	−150.09	34.23
	308.15	25.78	−47.41	−152.78	34.20
	313.15	25.53	−49.54	−156.26	34.08
0.072	298.15	22.30	−42.57	−133.99	30.66
	303.15	22.18	−43.99	−136.76	30.60
	308.15	22.08	−45.55	−139.69	30.55
	313.15	21.98	−47.20	−142.61	30.47
0.117	298.15	19.34	−42.35	−125.78	27.98
	303.15	19.25	−43.93	−128.60	27.93
	308.15	19.18	−45.63	−131.58	27.89
	313.15	18.95	−47.58	−134.68	27.81

Table 4. Values of constants, A, B and C of eq. (11) for S.D.S., C.T.A.B., SDS and C.T.A.B in presence of pyrosulphate ion at different temperatures

	10^7A	10^7B	10^7C	10^7A	10^7B	10^7C
	(T = 298.15)			(T = 303.15)		
SDS	16.89	−56.16	62.88	16.63	−55.27	61.84
SDS/$S_2O_7^{2-}$	26.99	−90.69	101.45	26.55	−89.17	99.74
CTAB	22.03	−71.80	80.56	21.73	−70.68	79.03
CTAB/$S_2O_7^{2-}$	31.24	−101.46	113.51	30.73	−99.82	111.71
	(T = 308.15)			(T = 313.15)		
SDS	16.40	−54.49	61.19	16.18	−53.77	60.33
SDS/$S_2O_7^{2-}$	26.13	−87.74	98.22	25.71	−86.36	96.80
CTAB	21.47	−69.85	78.28	21.23	−68.84	76.83
CTAB/$S_2O_7^{2-}$	30.24	−98.16	109.70	29.76	−96.77	108.59

Table 5. Values of constants, A' and B' of eq. (12) for S.D.S., C.T.A.B., SDS and CTAB in presence of pyrosulphate ion in water and water + acetone ($X_{acetone}$ = 0.016, 0.033, 0.072 and 0.117) mixtures

	$10^7A'$	$10^9B'$	$10^7A'$	$10^9B'$	$10^7A'$	$10^9B'$
	($X_{acetone}$ = 0.00)		($X_{acetone}$ = 0.016)		($X_{acetone}$ = 0.033)	
SDS	30.95	−4.72	19.30	−2.92	15.84	−2.38
SDS/$S_2O_7^{2-}$	52.39	−8.52	32.51	−5.26	26.54	−4.26
CTAB	37.87	−5.32	23.52	−3.20	19.37	−2.60
CTAB/$S_2O_7^{2-}$	60.63	−9.86	38.53	−6.26	32.03	−5.20
	($X_{acetone}$ = 0.072)		($X_{acetone}$ = 0.117)			
SDS	11.60	−1.70	8.68	−1.22		
SDS/$S_2O_7^{2-}$	19.57	−3.12	14.78	−2.32		
CTAB	14.41	−1.88	11.25	−1.46		
CTAB/$S_2O_7^{2-}$	24.40	−3.98	18.96	−3.06		

The negative values of ΔG^0 and ΔH^0 (Tables 1–3) indicate that the adsorption of the surfactants is stabilized and the process is exothermic in nature. The increasingly negative values of ΔG^0 and ΔH^0 in presence of $S_2O_7^{2-}$ at all temperatures and in all solvents indicate the increase in the extent of stabilization. The positive ΔS^0 values (Tables 1–3) are the indicative of desolvation effect. It is a fact that the adsorbed molecules loose freedom of translation associated with negative ΔS^0 values. As desolvation entails an increase in disorder due to more freely movable water molecules which might compensate for the decrease of ΔS^0 due to adsorption, the positive ΔS^0 values obtained in the present case point to the fact that the adsorbed molecules undergo desolvation on the surface region. The increase in the ΔS^0 values of the surfactants in presence of $S_2O_7^{2-}$ may be attributed to greater desolvation of the molecules in the same direction.

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Appendix A. Notation

$a_{\pm}$ Mean ionic activity,

I Ionic strength of the solution,

m Stoichiomolality,

R Gas constant per mole,

S Debye-Hückel constant,

T Temperature in kelvin,

z_+ Valency of the positive ion,

z_- Valency of the negative ion,

τ Thickness of the surface phase existing in equilibrium with the bulk phase,

ΔH^0 Standard molal enthalpy change,

ΔG^0 Standard molal Gibbs free energy change,

ΔS^0 Standard molal entropy change,

A,B,C Constants of eq. (11),

A',B' Constants of eq. (12).

Greek letters

α Degree of dissociation,

γ Surface tension of solution,

$\gamma_{\pm}$ Mean ionic activity coefficient.

Γ_2 Surface excess,

ν_+ Number of moles of positive ions given by 1 mole of the solute,

ν_- Number of moles of negative ions given by 1 mole of the solute.